

# **ACID RAIN**

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## **PREFACE**

The day to day relevance of Chemistry to the critical issues facing the human kind do not often get highlighted substantially in chemistry textbooks themselves, because of several constraints connected with textbook development. Thus, with the objective of generating greater awareness for the role of chemistry in such critical issues, the Department of Education in Science and Mathematics (DESM) of the National Council of Educational Research and Training (NCERT) has undertaken a project on 'Development of Modules in Chemistry on Some Current Topics of Human Concern'. Under this project, modules have been developed on selected topics, for teachers and students of senior secondary classes, which could also be of interest to others who wish to know about such issues. The first module developed, entitled 'Ozone Hole', discusses the phenomenon of depletion of the ozone layer and its consequences. The second module developed, entitled 'Greenhouse Effect and Global warming', deals with the phenomenon of greenhouse effect and its major consequence - global warming. The present module is the third in the series and deals with the phenomenon of acid rain.

Starting out with the meaning of the term acid rain, the booklet goes on to briefly discuss how acid rain is formed; its effects on the ecosystem, on human health and on structures. This is followed by a brief discussion on how the problem can be tackled technologically and how it is being actually tackled by national and international agencies. The 'Taj issue' - i.e. the debate on whether there is a possibility of the Taj being affected by the nearby Mathura Refinery has also been touched upon briefly. A detailed reference to literature cited in the text appears at the back of the booklet - to help those who may be interested to know more about the phenomenon of acid rain.

The author is thankful to Prof. A. N. Maheshwari, Joint Director, NCERT and to Prof. K.V. Rao, Head, DESM for their support to the project. The author is grateful to Prof. B. L. Khandelwal, I.I.T., Delhi, Dr. S. K. Wig, St. Stephen's College, Delhi, Dr. P. S. Jaiswal, Hansraj College, Delhi; Dr. S. Bhanumati, Gargi College, New Delhi and Dr. Jaishree Sharma, Reader, DESM for their critical comments on the first draft of the material.

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## **PREAMBLE**

The original module on 'Acid Rain' as produced in 1994 under a Project entitled 'Development of Material in Chemistry on Some Current Topics of Human Concern' of the Department of Education in Science and Mathematics (DESM) of the National Council of Educational Research and Training (NCERT). In the last decade, the phenomenon of Acid Rain has gained much importance for human kind in general and scientists in particular.

A decade later, the module is being revised and wherever possible new data and information added.

**M Chandra**  
**Professor DESM**

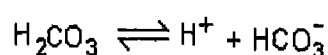
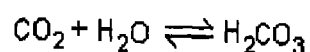
June 2004

In 1872, Robert Angus Smith, a British Chemist discovered a link between acid in rain falling near Manchester (U.K.) and the sulphur dioxide (SO<sub>2</sub>) given off when coal was burnt. It was then, that the term 'acid rain' entered the English language for the first time, when he used this term in his landmark book – 'Air and Rain. The beginning of Chemical Climatology'. He had used this term because he found it convenient, and dramatic - though not altogether accurate. 70 years later, research in Europe confirmed this discovery. Sulphur dioxide and nitrogen oxides produced (along with carbon dioxide and other gases) when oil, coal, natural gas or peat are burnt, can be converted in the atmosphere into acids which can return to earth in contaminated rain, snow, hail, fog or mist (1). Acid Rain emerged as a public concern for the first time, in 1972, at the 'United Nations Conference on Human Environment', in Stockholm, largely in response to a Swedish study. A number of major research efforts were also initiated in other countries to address the cause of acid rain deposition as well as its direct and indirect ecological effects (2)

In the strictest sense, acid rain (or more precisely 'acid deposition' or 'acid precipitation') means exactly what the term implies - rain which is more acidic\* than normal. In practice however, the term acid rain has expanded to cover the 'net deposition' of all acids, whether rain has been the vehicle for deposition or not. The net deposition of acids in sensitive areas may occur by snow or by 'occult' deposition by fog or mist. The term 'acid rain' also covers the direct 'dry' deposition of acid forming substances. Thus, the term acid rain now effectively covers all air pollution, which derives from potentially acid forming substances. (4)

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\* Due to dissolution of natural carbon dioxide present in the atmosphere 'pristine rain', i.e. rain uncontaminated by any anthropogenically (i.e. due to human activity) generated acid producing substance is found to have a pH of 5.6 and thus is acidic. The pH of 'natural' rain can be calculated from the following equilibrium



Based upon the concentration of CO<sub>2</sub> (g) normally found in the atmosphere (0.003 atm), the pH of pristine precipitation has been calculated to be 5.6, (3)

Removal from, and return back to the earth's atmosphere of substances that are themselves acid or can be converted to acids (and then to substances that can be removed from the atmosphere) is a natural process - and is part of the natural cleansing of the atmosphere. Without this cleansing process, (i.e. if the acidic substance once in the atmosphere just remained there), the atmosphere would have high degree of pollution.

However, in the down wind from industrial areas, most acid depositions result from industrial activities. Acid deposition can occur hundreds or thousands of miles away from the source of the pollutants and the substance emitted can be transformed within the atmosphere to new forms that results in greater acidity (5). It is this phenomenon of 'unnaturally acid' deposits whether 'wet' or 'dry' which has taken the general form of acid rain and is turning out to be a great source of concern for chemists, environmentalists, doctors and the public in general. Whereas, 'natural' rain has a pH of 5.6, rains in some parts of the U.S.A. has been measured to have a pH of 4.0 to 4.5\*

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\* To put these values in perspective, one could note that vinegar has a pH of 2.7 and milk a pH of 6.6 (Fig. 1). Acid rain with a pH of 4.5 to 4.0 is about 100 times more acidic than milk, but 100 times less acidic than vinegar (6).

## pH Values of a Number of Common Substances

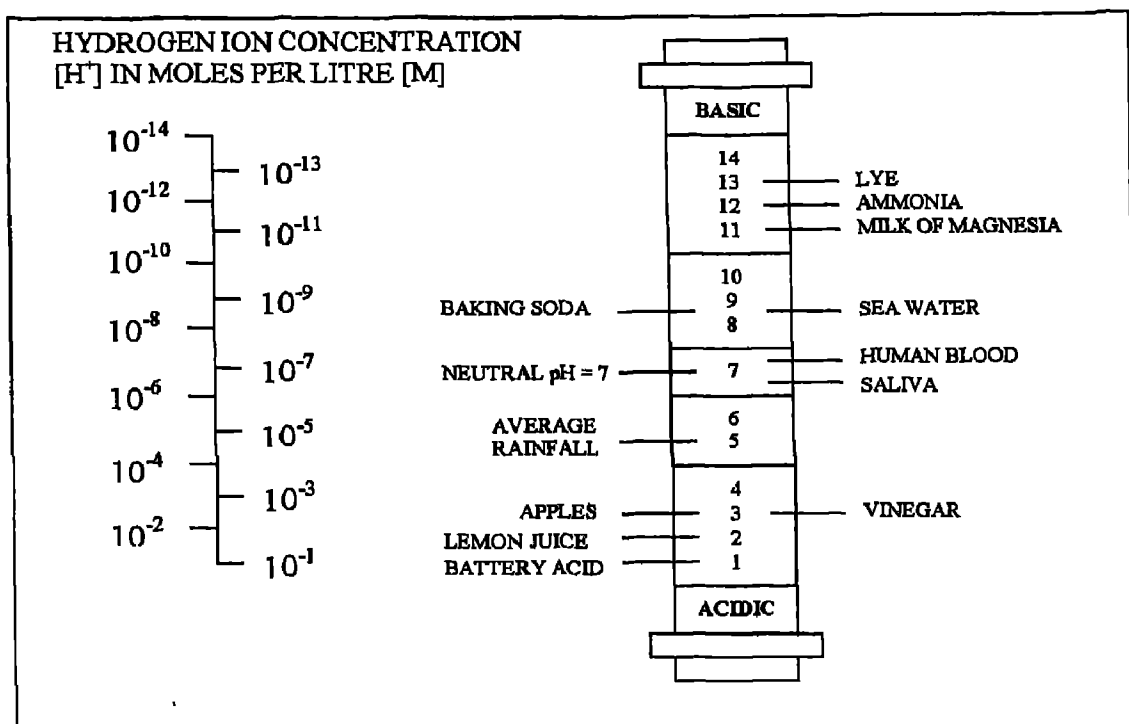


Figure 1.

Source JACOB (A.T.) Acid Rain Institute for Chemical Education (1991) 57 pp



## **WHAT CAUSES INCREASED ACID FORMATION IN THE ATMOSPHERE?**

Unnaturally acidic rain is a by-product of a variety of human activities that emit to the atmosphere nitric oxide (NO), nitrogen dioxide (NO<sub>2</sub>), sulphur dioxide (SO<sub>2</sub>), to some extent ozone (O<sub>3</sub>), and specially in the tropics -methanal (HCHO) and methanoic acid (HCOOH) (Table 1) NO reacts in air to form NO<sub>2</sub> and it is not easy to measure the concentration of these two gases independently NO and NO<sub>2</sub>, are usually referred together as NO<sub>x</sub>. These pollutants are converted into more acidic substances NO<sub>x</sub> into nitric acid (HNO<sub>3</sub>) and SO<sub>2</sub> into sulphuric acid (H<sub>2</sub>SO<sub>4</sub>), by processes, which are discussed later (see pages 11-14) NO<sub>x</sub> and SO<sub>2</sub> are often referred to as primary precursor pollutants.

Atmospheric acid can return to the planet in other forms besides rain NO, NO<sub>2</sub> or SO<sub>2</sub>, can be converted to stronger gaseous acids and such gases can be deposited directly onto soil, plants or water The primary pollutants can combine with tiny solid particles suspended in the atmosphere (atmospheric particulates), which ultimately precipitate onto earth's surface: SO<sub>2</sub> can return to the surface chemically unaltered and later react to form a stronger acid. Collectively these processes are called dry deposition Acids can also be formed and then deposited in aqueous form such as snow, rain, hail or sleet This is called wet deposition Finally at high elevation, the acids can return as fog in a process called droplet deposition. Often acid concentration is higher in fogs than in precipitates (7)

**Table 1**

### **SOURCES OF SO<sub>2</sub>, AND NO<sub>x</sub>**

- (i) generation of electricity,
- (ii) smelting and refinement of metals,
- (iii) production and use of concrete, glass, ceramics, plastic materials,
- (iv) refinement and use of petroleum and petrochemicals,
- (v) use of transportation vehicles,
- (vi) domestic and water heating,
- (vii) decomposition and incineration of sanitary and solid wastes,

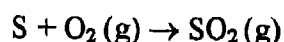
- (viii) production and application of fertilizers, pesticides and other agricultural and sericultural activities,
- (ix) decomposition of excreta of human and domestic animals,
- (x) burning of biomass, farm and forest residues,
- (xi) use of explosive devices in peace and war.

Source RODHE (H) et al Acidification in the Tropical Countries John Wiley (1988) 405 pp

### **SOURCE OF ACID FORMING GASES: (SO<sub>2</sub>), (NO<sub>2</sub>), (O<sub>3</sub>), (HCHO), (HCOOH)**

SO<sub>2</sub> All plants and animals contain some sulphur absorbed from their environment Several hundred million years ago, fossil fuels were formed when dead animals and plants decomposed and were broken down into liquid (oil), gases (natural gas) and solids (coal and peat). In the same swamps and sediments, mineral sulphides were formed, probably by bacteria, and by other processes

When sulphide ores are smelted (roasted) for metal extraction, SO<sub>2</sub> is emitted, and when fossil fuel is burnt, the long stored sulphur is also released as SO<sub>2</sub>. The sulphur content of oil and coal varies, depending largely on where it comes from Crude oil may have anything from 1% to 3% of sulphur according to geographic location of the oil, coal by contrast can have a sulphur content of anything from 0.4 to 5% and by no means uniform According to source, sulphur content varies from one grade to the next, and even from one seam to the next in the same mine, reflecting local variation in ecological condition millions of years ago 'Hard' coal such as anthracite is normally low in S, while 'soft coal' (bituminous semi-bituminous, lignite and brown coal) can contain much higher percentage of sulphur (8) (Table 2)

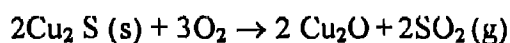


The same reaction occurs when diesel fuel which also contains sulphur burns In smelters, the sulphide ores combine with oxygen from air to form SO<sub>2</sub>

**Table 2**  
**AMOUNT OF SULPHUR IN FUELS GIVING SO<sub>2</sub> GAS**

SUBSTANCE	%
Wood	0
Peat	1
Lignite	1.3
Bituminous	1.6
Semi bituminous	1.2
Anthracite	1.0
Coke	1.0
Crude oil	0.5 – 3.0
Fuel oil	2 – 4
Natural gas	Trace

Source. HOPKAR (S.M.) Environment Pollution Analysis, Wiley Eastern Ltd (1993) 405 pp



Because metal ores contain much higher percentage of sulphur than does coal, the concentration of SO<sub>2</sub> emitted is greater from smelters than that from power plants. But since much more coal is burnt in power plants, pollution from power plants is greater. The major source of non-natural SO<sub>2</sub> is thus power plants, smelters, heavy industries, transportation industries - specially those which burn diesel (Table 3)\*

There are several natural sources of SO<sub>2</sub> also, e.g. the volcanoes. Salt marshes and swamps also emit sulphur containing compounds as a result of microbial activity. These include, apart from sulphur dioxide, hydrogen sulphide (H<sub>2</sub>S), dimethylsulphide [(CH<sub>3</sub>)<sub>2</sub>S]. The latter two compounds are responsible for the rotten egg smell and often they are quickly oxidized to SO<sub>2</sub> in the atmosphere. The quantity of SO<sub>2</sub> from natural source in the atmosphere is difficult to assess.

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\* Some representative data for India are given in Tables 4 & 5

It is important to realise that natural sources are more evenly distributed worldwide, as opposed to human generated sources, which are concentrated in industrial centres. Further, emission of natural sources of SO<sub>2</sub> excepting volcanoes is generally deposited on the ground, near the point of origin, not transported over long distances. (9)

**Table 3**  
**SO<sub>2</sub> FROM ANTHROPOGENIC SOURCE (AVERAGE FOR THE WORLD)**

SOURCE TYPE	(%)
Hard coal combustion	60
lignite coal combustion	
coal cooked	
Petroleum refining	28.1
motor spirit	
light fuel oils	
petroleum coke	
Copper smelted	10.4
copper refined	
lead smelted	
zinc	
Sulphuric acid	1.5
pulp and paper	

Source: WARNECK (P) Chemistry of the Natural Atmosphere Academic Press (1988) 757 pp.

**Table 4**

**AVERAGE LEVEL OF SO<sub>2</sub> IN AIR IN SOME INDIAN CITIES**

	<b>CITY</b>	<b>SO<sub>2</sub> (microgram/cubic metre)</b>
1	Mumbai	48.1
2	New Delhi	44.4
3	Kolkata	33.0
4	Kanpur	16.0
5	Ahmedabad	12.7
6.	Chennai	0.3
7	Nagpur	8.7
8	Hyderabad	6.1
9.	Jaipur	5.2

Source SWAROOP (R) et al Environment Pollution Analysis Mittal Publication (1992) 299pp

**Table 5**

**PERCENTAGE OF SO<sub>2</sub> EMITTED FROM DIFFERENT SOURCES IN MUMBAI**

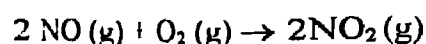
<b>SOURCE</b>	<b>%</b>
Industrial	68.8
Power house	18.0
Transportation	11.8
domestic	0.8
Others	0.6
Total	100.0

Source NEERI Annual Report (1993-94)

NO<sub>x</sub> NO<sub>x</sub> is emitted both by human activities and by natural process Combustion, whether in transportation or in electrical utilities is the human activity that produces most of the NO<sub>x</sub> During this, heated air which contains both nitrogen and oxygen form NO and to a small extent NO<sub>2</sub>.



This is an equilibrium reaction, NO molecules can also give back to form nitrogen and oxygen For this reaction the greater the temperature, the larger the equilibrium constant and greater the concentration of NO. If a high temperature mixture of gases is cooled rapidly (as when combustion gases are emitted from automobiles or from furnaces), the rate at which NO gives back nitrogen and oxygen, becomes very slow. Thus controlling the maximum temperature of combustion gases and their rate of cooling can reduce emission. Once NO is formed in the combustion process, it can react to form NO<sub>2</sub> and so both oxides are emitted



Average emission rates of NO<sub>x</sub> from transport vehicles are lowest when the speed of a vehicle is between 25 to 50 km/h, but rises with increase of speed (Table 6). High NO<sub>x</sub> emissions are also produced during periods of rapid acceleration

**Table 6**  
**RELATION OF NO<sub>x</sub> EMISSION AND SPEED**

SPEED (km/h)	NO <sub>x</sub> EMISSION g/km
10	2.53
25	2.17
50	2.13
75	2.24
100	2.07
125	4.15
150	6.07

Source WATKINS (L.H.) Air Pollution from Road vehicles HMSO (1991) 152 pp

O<sub>3</sub> When the air temperature is  $> 15^{\circ}\text{C}$ , the  $\text{NO}_x$  and unburnt hydrocarbon in vehicle exhaust gases can react in prolonged strong sunlight to form ozone ( $\text{O}_3$ ), which in turn is involved in the conversion of  $\text{SO}_2$  and  $\text{NO}_x$  to acids. The formation of human made  $\text{O}_3$  has increased enormously with the rising levels of  $\text{NO}_x$  in the atmosphere. Until recently, relatively little attention was paid to the role of  $\text{O}_3$  in air pollution, beyond its well known and well documented effects during photochemical smog in urban areas. But  $\text{O}_3$  is now being recognized as a major factor in the formation of acid pollutants. (11)

HCHO and HCOOH\* Methanal (formaldehyde) contribute to acid rain in the tropical ecosystem. Formate is reported to be a contributing factor for acid rain in countries such as Venezuela. The atmospheric source of methanoic acid in rain has not been well established. The most likely sources are scavenging of gaseous acid by cloud water and in-cloud production of methanoic acid from methanal oxidation. It is known that biomass burning causes emissions of methanoic acid and methanal. (12)

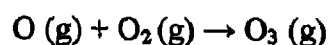
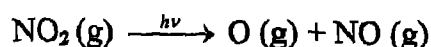
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\* Contribution of  $\text{SO}_2$  and  $\text{NO}_x$  to acid rain being larger than that of  $\text{O}_3$ , methanal or methanoic acid. The discussions later on will be restricted to  $\text{SO}_2$  and  $\text{NO}_x$  only.

## CONVERSION OF SO<sub>2</sub> AND NO<sub>x</sub> IN THE ATMOSPHERE TO ACIDS

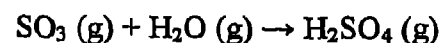
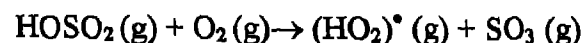
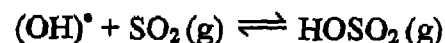
SO<sub>2</sub>. Pathways for the oxidation of SO<sub>2</sub> in the atmosphere are complex and have not been fully delineated. The reaction occurs in gas phase, in fog and on cloud droplets on the surface of aerosol particle\*. (13)

There are two overall processes that convert SO<sub>2</sub> to sulphuric acid (H<sub>2</sub>SO<sub>4</sub>). One takes place in the gas phase and involves oxidation of SO<sub>2</sub> by hydroxyl radical (OH)<sup>\*</sup>, the other takes place in liquid droplets, where oxidation is carried out by hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) (OH)<sup>\*</sup> can be produced by a series of reactions:



(where O<sup>\*</sup> (g) denotes an excited oxygen atom)

The gas phase oxidation of SO<sub>2</sub> then follows as:



The above however represents only one of the several mechanisms for the oxidation of SO<sub>2</sub> to H<sub>2</sub>SO<sub>4</sub>.

The mechanism involving H<sub>2</sub>O<sub>2</sub> is currently considered to be a dominant mechanism, where H<sub>2</sub>O<sub>2</sub> is taken to produce by a sequence of reactions that begin when (OH)<sup>\*</sup> (g) reacts with CO<sub>2</sub> (g) The H<sub>2</sub>O<sub>2</sub> dissolves in a water droplet and then reacts with HSO<sub>3</sub><sup>-</sup> ·

$$\text{HSO}_3^- + \text{H}_2\text{O}_2 (\text{aq}) \rightleftharpoons \text{HSO}_4^- (\text{aq}) + \text{H}_2\text{O} (\text{l})$$

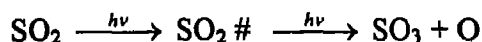
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\* Aerosols are colloidal systems in which liquid or sometimes solid particles with a diameter measuring 10<sup>-2</sup> mm to 10<sup>-6</sup> mm are distributed in a gas phase (such as air)



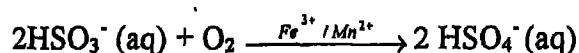
Another mechanism suggested has been the oxidation of  $\text{HSO}_3^-$  by  $\text{O}_3$  in water at  $\text{pH} > 5$ . All these oxidation mechanisms can occur simultaneously, though conditions at any time may favour one over another (14).

The direct gas phase photo-oxidation of  $\text{SO}_2$ :



is a slow process, because the excitation energy is mainly lost in collision with air molecules rather than being utilised to convert  $\text{SO}_2$  to sulphurtrioxide ( $\text{SO}_3$ ). Therefore, the most important oxidation reaction is taken to be that initiated by radicals - the best known being the reaction of  $\text{SO}_2$  with  $(\text{OH})^\cdot$  as explained earlier. Peroxyradicals such as  $(\text{HO}_2)^\cdot$ ,  $(\text{CH}_3\text{O}_2)^\cdot$  etc appear to be potentially less effective in oxidising  $\text{SO}_2$ .

In the presence of clouds, fogs,  $\text{SO}_2$  dissolves to some extent in liquid water, where it forms  $\text{HSO}_3^-$  and  $\text{SO}_3^{2-}$ . These ions are subjected to oxidation by  $\text{O}_2$ ,  $\text{O}_3$  and  $\text{H}_2\text{O}_2$ . The direct reaction with  $\text{O}_2$  is slow and could be ignored, but it is catalysed by the ions of heavy metals such as Fe and Mn:



The source of these elements in cloud and fog water droplets is the mineral fraction of aerosol particles that serve as cloud condensation nuclei (15)

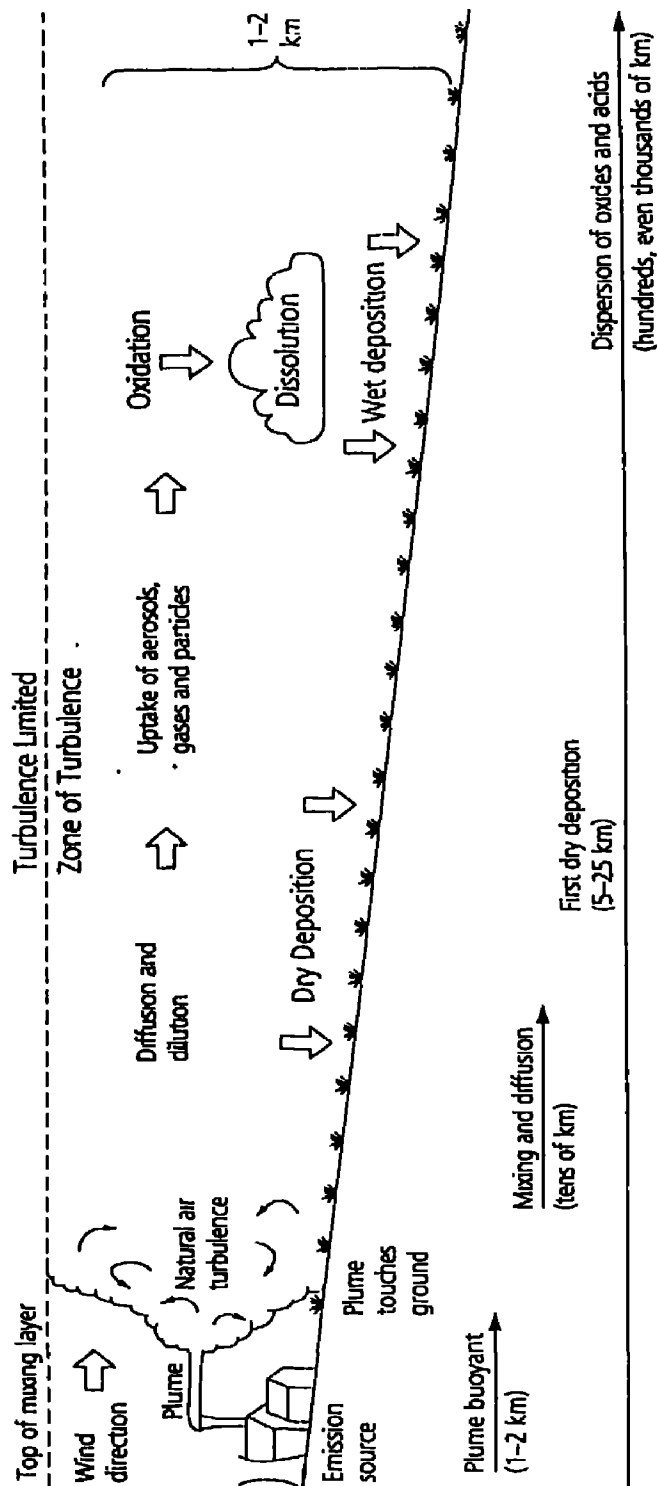
In the absence of sunlight, specially if plenty of water is present, the aqueous phase reaction becomes important in oxidising  $\text{SO}_2$  to  $\text{H}_2\text{SO}_4$



Since the major source of  $\text{SO}_2$  emission to the atmosphere is the electric power generating units, considerable research has been done with regard to plumes from chimneys of power generating stations. There is evidence to show that  $\text{SO}_2$  conversion rate undergoes a diurnal cycle, with maximum value occurring at midday and minimum rate at nights. Seasonal variations of the conversion rate show a maximum in summer and a minimum in winter - showing the importance of the photochemical mechanism.

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\*  $\text{HSO}_3^-$  can be oxidized to  $\text{HSO}_4^-$  in a variety of ways as stated above.



**Figure 2.1** Dispersion and deposition of acid substances. Sulphur dioxide and nitrogen oxides are released from point sources, then dispersed as winds blow the gases downwind. Some of the acidic material is deposited as gases, particles and aerosols quite close to the emission source, but most is blown long distances, converted and washed out of the atmosphere as wet deposition. SOURCE: PARK (c). THE ENVIRONMENT (2004) 660 pp.

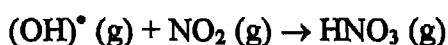
Research on plumes from urban sources other than the powerhouse plumes show that in many cases the conversion rate is considerably high for such urban plumes. Since such plumes come in contact with the ground surface more readily, dry deposition of  $\text{SO}_2$  on the ground is also unavoidable. (17)

The wet deposition of  $\text{SO}_4^{2-}$  from the atmosphere may occur through distance types of processes – ‘rainout’ and ‘washout’. Rainout is believed to be more significant source of wet deposited sulphate at some distance from the emission source, while washout may predominate at shorter ranges. ‘Rainout’ involves the deposition of water droplets already containing sulphur compounds. ‘Washout’ of sulphur compounds occurs when falling rain passes through polluted air. Heavy rain, with large droplets is less likely to capture  $\text{SO}_2$  or sulphate aerosol from the atmosphere in this way.

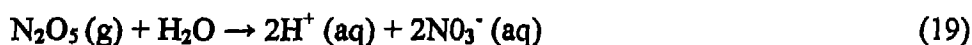
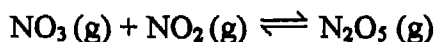
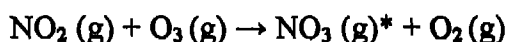
Wet deposition of sulphur compounds tends to be episodic. Measurements have shown that about half the annual sulphate may be deposited in only 8-9 days. This may have important implications in terms of damaging effects (18)

$\text{NO}_x$ : The oxidation of  $\text{NO}_2$  to  $\text{HNO}_3$  occurs in two ways.

One way is by direct reaction with  $(\text{OH})^\bullet$  radical



The other way is by indirect reaction with  $\text{O}_3$ .



In absence of sunlight, the dominant reaction is



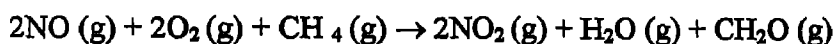
During combustion, the primary nitrogen oxide produced is  $\text{NO}$ . Some reaction (or reactions) converts  $\text{NO}$  to  $\text{NO}_2$  before the above reactions can take place. The most important of these processes is catalysed by  $\text{HO}$  and  $\text{HO}_2$  and involves volatile organic compounds, which include methane ( $\text{CH}_4$ ), butane ( $\text{C}_4\text{H}_{10}$ ), octane ( $\text{C}_8\text{H}_{18}$ ). They are released to the atmosphere by incomplete combustion or by evaporation of solvents or

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\*  $\text{NO}_3$  is highly unstable

fuel from industries, from automobiles by natural process such as emission from evergreen trees

A typical example of such a reaction is:



There are other mechanisms also that oxidise NO to NO<sub>2</sub>, but these are of lesser importance.

There is considerable regional variation in relative quantities of acid deposition derived from nitrogen versus sulphur. Once emitted to the atmosphere, about 5% of the available SO<sub>2</sub> can be chemically converted to H<sub>2</sub>SO<sub>4</sub> / hour while approximately 20% of the available NO<sub>x</sub> can be converted to HNO<sub>3</sub> / hour. Because its oxidation is slower, SO<sub>2</sub> can travel further than NO<sub>x</sub> before returning to the surface as an acid. HNO<sub>3</sub> travels much less from its origin because of the shorter time needed to convert NO<sub>x</sub> to HNO<sub>3</sub> and the lower height of the emission source. (21)

**Table 7**

**Emission of SO<sub>2</sub> and NO<sub>2</sub> in India ('000 tonnes )**

<b>Sector</b>	<b>SO<sub>2</sub></b>	<b>NO<sub>2</sub></b>
<b>Industrial</b>	<b>243.0 (4)</b>	<b>126.0 (4.9)</b>
<b>Household</b>	<b>4898.1 (81.5)</b>	<b>992.5 (38.5)</b>
<b>Transport</b>	<b>306.0 (5.1)</b>	<b>694.6 (27.0)</b>
<b>Power</b>	<b>565.0 (9.4)</b>	<b>765.0 (29.7)</b>
<b>Total</b>	<b>6012.1</b>	<b>2578.1</b>

Numbers in bracket show %

Source. KADEKODI (G K.) et al Environment Economics in Practice. OUP (2004) 372 pp.

**EFFECTS OF ACID RAIN:**

The environmental effects of acid deposition depends on whether it is dry or wet, and on the level of contact it has with plants, water courses and buildings. Three levels of receptors of acid pollution have been identified:

The primary receptors experience direct contact with atmospheric pollutants, e.g. the outer surface of buildings, trees and plants

The secondary receptors experience contact with pollutants only after they have been in contact with other materials, e.g. the inner foliage of plants or the soil beneath vegetation

The tertiary receptors are indirectly affected by pollutants e.g. subsoil bedrock, water courses and lakes that receive most of their water from run-offs

Dry deposits have several direct effects on the environment. It attacks and corrodes buildings, metals, stone and even leather, paper and textiles. It is deposited on forests and farmlands, affecting plant growth and crop yields. It mixes fog and dust to create 'smog' that can cause respiratory problems among susceptible people and animals.

Wet deposition has both direct and indirect effects. It increases the acidity of lakes and rivers, which is made worse by the inflow of acids and metals from the nearby soils. The effects vary depending on the volume of deposit and inherent sensitivity of the soil and water. Aquatic species die, making the lakes and rivers too barren to support fish life. Wet deposit can transport metals viz. aluminum, cadmium, mercury into soil, groundwater, lakes and streams depleting the stock of nutrients in the soil and weakening plants. It has been implicated in reducing crop yields and in corroding buildings and structures. More controversially, it has been alleged to aggravate heart and lung diseases in humans.

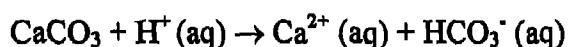
Although the damage attributed to acid rain is both visible and invisible, in each case, understanding the chemistry involved helps understand approaches by which environmental damages can be minimized.

Soil Apart from the factors due to acid rain, soil acidification due to anthropogenic reasons comes from several sources. Modern agriculture and forestry techniques produce an imbalance between the production and consumption of  $H^+$  in the ground. Many of the commercial fertilizers being ammonia based, release  $H^+$  and promote acidification. Agricultural intensification may also have an effect by removal of plant mass from the ground. The more plant mass is removed, the less the soil is able to neutralise the  $H^+$  brought by air pollution and inflowing water. As acid rain increases the input of  $H^+$  to the soil, the rate of cation exchange increases. Once displaced, the cation

can be leached down through and out of the soil. Thus, a sign of necessary soil and ground acidification is a rising level of cation content in the groundwater (22). Another acid producing process is the leaching of organic acids from plant litters. This process is particularly important for coniferous trees, which have been identified as major cause of soil acidification. (23)

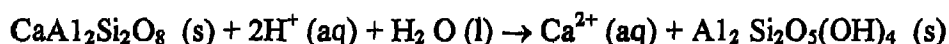
In case of acidification due to acid rain, once the acid rain enters the soil, its impact will depend very much on the soil type and the underlying bedrock. Therefore, a definite description of how acids react with soil is difficult because each soil system is different. In general, there are 2 major processes: adsorption and dissolution. In the adsorption process, the incoming acids are physically trapped by organic matter by adsorbing the  $H^+$  ions. Also, depending on the type and quantity of plant life present, the  $H^+$  ions are adsorbed into mineral hydroxides and oxides, in the process releasing cations, usually  $Na^+$ ,  $K^+$ ,  $Ca^{2+}$  and  $Mg^{2+}$ .

For soil that was originally neutral or basic ( $pH = 7$  or above), the first reaction that occurs after acidic deposition, is dissolution of carbonate minerals, such as calcite ( $CaCO_3$ ) or magnesium carbonate ( $MgCO_3$ ).



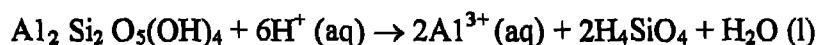
In the mineral form  $Ca^{2+}$  and  $CO_3^{2-}$  were immobilized, i.e. they were trapped as a solid with the soil, but after reacting with acids, the ions are mobilized and are carried along with water as it percolates through the soil. The ions might eventually even leave the soil system and thus become unavailable to plants.

As the pH is lowered below 7, calciumaluminosilicate minerals, such as anorthite ( $CaAl_2Si_2O_8$ ) reacts with acids:

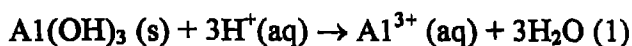


In pH range between 5 and 4.2, ion exchange can occur in which one cation is replaced by another, e.g.  $H^+$  replaces cation such as  $Al^{3+}$ ,  $Mn^{2+}$  of the soil.

At an even lower pH, more  $Al^{3+}$  is released either by the cation exchange process or by aluminosilicate dissolution.



As the pH drops below 4.2, other aluminum hydroxide minerals e.g.  $Al(OH)_3$  (gibbsite) start to dissolve.



As pH drops further and reaches below 3.8, iron minerals begin to react with the acids and iron is mobilized into the soil system (24). Acidification processes are often of an episodic nature, leading to 'acid flushes' and the episodes are generally associated with heavy rain (or sudden snow melt), which follows a long dry period. (25)

The acidification of soil can be delayed or prevented by protective neutralizing systems. While most soils have enough neutralizing capacity to offset the effect of acid rain, the chemical properties and stability of soils and soil ecosystems vary considerably. Their susceptibility to acidification depends on several factors: the type of bedrock, the kind of soil, the size of soil particles, and how the land is used

Soils have two main neutralizing systems: ion exchange and chemical weathering. The rate of ion exchange depends on the supply of cations. The fewer the number of cations, the lesser is the neutralizing ability (26). The weathering of bedrock material underlying soil system is the other major (but much slower) acid neutralizing process.

Bedrock is available in enormous quantities in comparison to annual deposited acidity. A 1 mm layer is capable of absorbing hundreds even thousands of years of  $\text{H}^+$  deposition at the current rates. However, bedrock weathering is limited by the rate of the chemical reaction and the limited amount of soil moisture which ever comes into contact with it (27).

Streams and lakes: Acid deposition can enter streams and lakes directly as wet or dry deposition or indirectly as drainage or snow melt after passing through the forest canopy and soil. If the lake water or sediment contains minerals that can react with the incoming acids, the lake pH can be maintained for some time. As a result of these reactions, base cations or other (often toxic) metal ions are mobilized from the lake or streambed. Shifts can occur in the relative concentration of biologically significant ions such as  $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{PO}_4^{3-}$  and  $\text{Mg}^{2+}$ . Toxic metal ions such as  $\text{Pb}^{2+}$ ,  $\text{Hg}^{2+}$  and  $\text{Al}^{3+}$  begin to be released into the water. Eventually lakes' ability to absorb the acidic inputs is saturated and pH decreases.

There can be a wide disparity in the acidity and metal ion concentration at the inlets and outlets of lakes depending on the individual feeder stream and the stream-bed neutralizing capacities. Differences in pH can occur at different depths, since water from

cooler feeder stream may flow to deeper levels. Temperature change that initiates lake mixing may also cause a sudden change in acidity or in metal ion concentration (28)

Several factors determine the susceptibility of lakes and water sources to acidification:

- i) One such factor is the neutralizing capacity of surrounding soils.
- ii) A second factor is the extent and volume of surface run off - the heavier the rain and the more impermeable the ground, the greater the volume of runoff and less time the water will have to permeate the ground and be neutralized. Rain storms following extended dry periods can wash off sulphates present due to dry deposition, or formed due to oxidation of sulphide materials during the dry spell.
- iii) The third factor that determines the susceptibility of lakes and water sources to acidification is the size of the catchments area, the smaller the area, the shorter is the time before runoff water reaches the lake - and less time there is for the water to be neutralized.
- iv) Location of the water system also determines the susceptibility of lakes and water bodies to acidification. Lakes at high altitude are closer to the sources of streams, so the water emptying into them will have had less time to be neutralized.
- v) Humus present in the soil of the lake can both absorb  $H^+$  making the lake more alkaline, and also produce  $H^+$  making the lake more acidic depending on conditions prevailing.

There are three stages of acidification of surface water. In the first stage, the  $HCO_3^-$  present in the lake due to bedrock and soil surrounding the lake neutralizes acids by reacting with  $H^+$  to produce  $CO_2$  and  $H_2O$ . As long as the  $HCO_3^-$  content is maintained at a crucial minimum level, the pH value of the water will remain stable, and plants, animals and microorganisms will be unaffected. But a lake or water-body subject to major acid inputs will be vulnerable.

In the second stage, the  $HCO_3^-$  content drops below the critical level and large influxes of  $H^+$  can no longer be neutralised. The pH value becomes unstable and begins to go down faster than before. Acid surges can drastically upset the delicate balance that remains. A sudden release of huge amounts of acidic water into the lake or water source, after heavy rain following a period of draught can be deadly, especially if it occurs when



the organisms are at the most sensitive part of their life cycle, e.g. for fish when they are young. The third stage comes when the pH value stabilizes around 4.5, regardless of new influxes of  $H^+$ . Almost all living systems - including many insects are eliminated, fish disappear and a small number of resilient animal and plant species predominate. An entirely new eco-system emerges. The water becomes abnormally clear - because the tiny plants that normally float on the surface of water, and the organic matter normally suspended in the lake, giving the lake a brownish surface, are both greatly reduced in density. It may be mentioned that, natural sources of acidity -  $H_2CO_3$  in rain and organic acids from humus decomposition can contribute to a background acidity of pH 5 in lakes, but are not by themselves enough to account for recent surges in acidity in lakes.

Acidity in water can release in soils metals like aluminum, cadmium, mercury, lead, arsenic - which go on to contaminate ground and surface water. Aluminium, one of the commonest elements on earth's crust, causes no harm to living organisms, as long as it is immobile. Once it reaches groundwater, (by processes as explained), damages the finer roots or filaments of plants and impedes the uptake of nutrients and water. It also interferes with the ability of plants to assimilate phosphorous - a plant nutrient, which gets tied up by free aluminium into almost insoluble aluminiumphosphate. Aluminium is also directly toxic to animals, mainly fish. Some kidney patients have apparently suffered speech and brain damage from aluminium contaminated water used in dialysis. Acidification releases cadmium from soils to water, which causes plants to take it up more readily. It reaches the human body through water and food and tends to concentrate mainly in the kidney. In acidified lakes, mercury is converted to methylmercury and becomes accessible to plants and animals through their food chain (29). In general, most fish perish and cannot reproduce if the pH of a lake dips below approximately 5. The biological response however, is a gradual one. Different species of aquatic plants and animals have different sensitivities and their responses to increased acidity, altered pattern of nutrients and mobilized toxic metal ions are also different. Though recent methods for determining the pH history of lakes have indicated that some lakes have been acidic (due to natural reasons) for thousands of years, vast majority of acidic lakes have had their pH lowered by acid pollution. There are two main ways of raising the pH of a lake - reducing the acidic inputs and if necessary neutralizing unwanted acids. These

goals can be achieved by reducing  $\text{SO}_2$  and  $\text{NO}_x$  emissions and by direct addition of bases, respectively. The most common form of direct neutralization of acids present in lakes is a method called 'liming' - adding limestone to the water. Limestone, which consists primarily of two minerals: calcite ( $\text{CaCO}_3$ ) and dolomite ( $\text{CaCO}_3 \cdot \text{MgCO}_3$ ) is used, because it is weakly basic and when properly applied, neutralizes without large swings in the pH. Also, limestone is preferred over soda ash ( $\text{Na}_2\text{CO}_3$ ), since limestone also injects into the water  $\text{Ca}^{2+}$ , which can alleviate toxicity increase due to  $\text{Al}^{3+}$  (30).

Forests. The scientific understanding of forest damage is much less complete than that of soil or surface water acidification. A variety of hypothesis, competing and complementary, exist to explain the various types of forest damage, which have been observed. According to an early hypothesis, soil acidification is taken to be the underlying cause of poor forest health, as aluminum leached from the soil damages the fine root system of trees and impedes the uptake of vital nutrients such as calcium, magnesium, potassium etc.

The 'multiple stress hypothesis' is another theory put forth for forest damage, according to which, a combination of ozone, acid mist and acid precipitation is taken to trigger severe damage of trees already stressed by soil acidification (31).

According to another theory, acid pollutants and oxidisers, most notably ozone, hydrogenperoxide ( $\text{H}_2\text{O}_2$ ) destroy cell membranes or the protective wax coating on leaves and needles. Once these are damaged, nutrients may leach away and plants become susceptible to diseases.

Sulphurdioxide, ozone and oxides of nitrogen are also found to enter leaves through the stomata (leaf pores), and ozone and sulphur dioxide are known to damage green chlorophyll pigments essential for photosynthesis. Laboratory experiments have shown that the pollutants have a synergistic effect. \*

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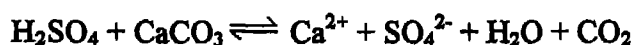
\* A synergistic effect is a phenomenon in which the effect of two or more substances taken together is greater than the sum of the effects each would cause separately (32)

It has been suggested that the build up of nitrogen in soils and plants as a direct result of atmospheric deposition could be an additional explanation for death of forests. Nitrogen in the form of ammonia or nitrate is an important plant nutrient. But most plants through evolution have adapted to be able to exist with very low level of nitrogen. The recent increase of available nitrogen in air has caused nitrogen over saturation, tree growth being accelerated and trees forming large cells that are easily attacked by land, droughts etc

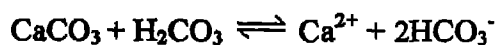
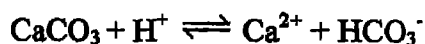
Human Health Sulphur dioxide is a relatively nontoxic gas compared to carbon monoxide and oxides of nitrogen. But high concentration of sulphur dioxide is known to cause respiratory problems in human beings. Thus, in the short term, health may be affected by breathing air, which is heavy in acid producing gases. In the long term also, health may be affected by breathing polluted air, even if in lower levels. Indirectly, acid pollution affects health by exposure to heavy metals or to aluminium released into soils and water as a result of acidification. The accumulation of metals in aquatic food chain or heavy metals dissolved in acid water supplied through lead or copper pipes may also result in health problems (33)

Structures / Monuments Theoretically almost every building either in or down wind of a major urban or industrial centre may be at the risk of corrosive action of acid deposition - whether dry or wet. However, structures, which show a high degree of effect due to acid deposition are those which are of marble (calcareous stone, made of large crystals of calcite, the thermodynamically stable mineral form of  $\text{CaCO}_3$ ). Chemically, marble and limestone are identical but they differ in crystal size and porosity. Limestone being made from smaller crystals is more porous than marble. This difference affects the appearance and “workability” of the stones. Pure sandstone (a sedimentary rock made of sand) and granite (a rock made of quartz, mica and feldspar) are not affected by acid rain.

The reaction between calcareous stone and acid rain can be written in the simplified form as



The reaction however is more involved than the one represented above, and evidence suggests that three reactions occur simultaneously:



The different mechanisms controlling the reaction of calcite depend on several conditions - pH, flow hydrodynamics etc. Since conditions can vary even on the surface of a single monument, several mechanisms can be operating simultaneously even on areas close to each other

The damage resulting from chemical reaction of calcite is mainly a surface phenomenon. This is of special concern when the details of the finely worked relief are only some centimeters in depth. The structural integrity of the marble structure are not affected however, by this surface reaction.

However, the problem of the deterioration is more complicated than this. The calcium sulphate ( $\text{CaSO}_4$ ) formed by the reaction of acid rain with calcite of the stone, as stated earlier, can crystallise as a dihydrate salt  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  (gypsum). This is somewhat soluble in water and therefore accumulates specially on those surfaces of the reacted stone, over which there is no direct substantial flow of water. Marble structures therefore develop a layer of gypsum in those areas protected from rain. Because of urban air pollution by dust particles, fly ash and other combustion products (dry deposit), this layer of gypsum blackens. After years in an urban environment, marble structures present a black and white appearance – white where the rain washes off the gypsum, black where the rain cannot wash away the dark gypsum layer.

Acid rainwater containing somewhat soluble sulphates and the soluble nitrates formed due to reaction with calcareous stones, penetrates the stone by capillary action. When the stone dries out the salts crystallize in the pore system. The pressure exerted by those crystallized salts is sufficient to disrupt the matrix of the stone mechanically. It is evident then, that the porosity of a stone is one of the important factors determining its durability, since it controls the amount of solution that will penetrate the pore system. The damage produced by this type of mechanical action can be more serious than that produced by simple chemical dissolution of the stone.

Thus, the deterioration of calcareous stone occurs mainly through two mechanisms.

- i) The chemical reaction of calcite
- ii) The mechanical damage produced when soluble salts formed during the reaction subsequently re-crystallize in pores of the stone

The first mechanism is important when surface details are to be preserved on the structure the second mechanism can contribute significantly to the structural degradation of the monument (34).

Pigments in paints can make paintwork susceptible to acid rain. Also, humidity encourages metal corrosion. An important factor is the delivery of moisture, gases and particles to the material surface. The physical location is important - the level of pollutants may for example be high at a lower level than at a higher level. A third major factor is the physical force of delivery of pollutants, which is determined by air temperature, wind speed (which for instance dries out wet surface more quickly and decreases rate of corrosion) and the intensity, direction and amount of rainfall (35) Table 8

**Table 8**  
**DAMAGE TO MATERIAL DUE TO ACID GASES**

<b>MATERIAL</b>	<b>TYPES OF IMPACT</b>	<b>PRINCIPAL POLLUTANT</b>
Metal	Corrosion, tarnishing	SO <sub>2</sub>
Building-stone	Surface erosion, soiling, black crust formation	SO <sub>2</sub>
Ceramics and glass	Surface erosion, crust formation	Different acid gases (specially fluorides)
Paints	Surface erosion, discoloration, soiling	SO <sub>2</sub> , H <sub>2</sub> S
Paper	Embitterment, discoloration	SO <sub>2</sub>
Photographic material	Small blemishes	SO <sub>2</sub>
Textiles	Soiling and reduced tensile strength	SO <sub>2</sub> and NO <sub>x</sub>
Textile dyes	Fading, change of colour	NO <sub>x</sub>

Source: MCCORMIK (J) Acid Earth. International Institute of Environment and Development (1985) 190 pp

#### **HOW CAN THE ACID EMISSIONS BE REDUCED?**

Efforts to control acid deposition have focused largely on cutting emission of sulphur dioxide, because sulphuric acid is a more important acidifying agent than are oxides of nitrogen. Once the latter have been converted to nitrates, they are rapidly absorbed by plants. (36)

Building smoke stacks higher and higher so that concentrated sulphur dioxide can disperse is no longer a solution when too many sulphur spewing stacks have already been built. Also, de-sulphurising by oil companies does not help the coal burning utilities. The best chance is to remove sulphur from the flue gas before it escapes from the stack (37)

There are four main routes to cutting polluting acid emission:

- i) using low pollutant fuel,
- ii) preventing the formation of pollutants during combustion,
- iii) screening pollutants from exhaust and flue gases,
- iv) energy conservation and use of non-conventional sources of energy

i) Use of low polluting fuels. (a) Using low sulphur coal is the simplest way of reducing sulphur emission from fossil fuel, but supplies of low sulphur fuel are limited and they are more expensive (38) (b) when use of low sulphur coal is found to be difficult, physical coal cleaning (PCC) techniques have also been used. This approach relies on the fact that coal has a low specific gravity than impurities such as sulphur associated with it (in the pyrite form). Thus the sulphur can be separated by washing coal in a water medium that allows the crushed coal to float and the impurities to sink. (39). However, removing organic sulphur from coal would require chemical or biological processing at a much higher cost. Thus, the PCC method is not very effective and is normally used in conjunction with other control options. PCC also produces a substantial amount of solid waste (40). (c) One apparently cheap and simple coal cleaning technique still in its experimental stage uses a dry electrostatic process. d) During refining of fuel oil, most of the sulphur in oil ends up in heavy oil fractions and this can be reduced by techniques already used by refineries. Indirect oil desulphurisation (or hydrodesulphurisation) is a simple and commercially well-established technique (41)

ii) Control during combustion: The newer power plant technologies offer comprehensive solutions and 'clean coal technologies' are already being demonstrated in full sized plants:

(a) In atmospheric fluidized bed combustion, a turbulent bed of pulverised coal and limestone is suspended by an upward blast of air. The combustion region is threaded with boiler tubes, which supply steam to the plants' turbines. The turbulent mixing of coal and air allows combustion to take place at a lower and more even temperature than it does in a conventional boiler, which reduces the formation of oxides of nitrogen. Meanwhile, the limestone effectively captures the  $\text{SO}_2$ . In the related technology of the pressurized

fluidized bed combustion, the coal is burnt in compressed air, which improves the plant's efficiency as well. In a third technique – the gasification/combined cycle, coal is reacted with steam and air at high temperature to produce a gas consisting mainly of hydrogen and carbon monoxide. Waste heat in the gas turbines' exhaust serves to yield additional electricity. It is for this reason, that it is called a 'combined cycle' (42)

b) The Lime Injection Multistage Burners (LIMB) technique: Control of sulphur dioxide and oxides of nitrogen emission is basically a combination of the low  $\text{NO}_x$  producing method, and a sulphur removal method. This method, still under development involves the use of staged combustion technique combined with limestone injection. Sulphur dioxide reacts with limestone to form solid calciumsulphate  $\text{Ca}(\text{SO})_4$ . LIMB is flexible and promises retrofitting. In fact, retrofitting of existing plants with flue gas desulphurisation (FGD) offers the fastest way to reduce power plant emission.

iii) Post Combustion Control: Flue gases can be treated (scrubbed) to make them clean, and controls can be applied to road vehicles to filter exhaust emission. FGD has been used commercially for several years and is the most immediate and widely used method for reducing sulphurdioxide emission. The scrubbing processes are broadly classified under two heads – (i) the wet processes (ii) the dry process. The wet scrubbing process is more widely used of the two. The types of wet scrubbing process in use are those using a recovery process, where the absorbent is regenerated and recirculated to the system, and those using non recovery methods using limestone, soda or dilute sulphuric acid as an absorbent to remove sulphur dioxide.

One natural criterion of a wet scrubber is that the absorbent should have a large capacity for absorbing sulphurdioxide at a fast rate so as to reduce the size of the equipment. Sulphurdioxide is slightly soluble in water, so use of water as an absorbent is ruled out. The most commonly used absorbents are.

- i) lime solution / limestone slurry
- ii) magnesiumoxide ( $\text{MgO}$ ) slurries/magnesiumhydroxide  $\text{Mg}(\text{OH})_2$  solution
- iii) sodiumhydroxide ( $\text{NaOH}$ ) solution
- iv) sodiumsulphite - sodiumbisulphite ( $\text{Na}_2\text{SO}_3 - \text{NaHSO}_3$ ) solution. Of these, use of limestone is the most predominant. (43) It can be used effectively by injecting it into



the furnace, where it calcines to lime and reacts with the sulphurdioxide, or it could be used in a scrubber - a type of a shower bath in which the liquid limestone slurry absorbs the sulphurdioxide initially to form calciumsulphite sludge ( $\text{CaSO}_3$ ) and carbondioxide gas. The  $\text{CaSO}_3$  sludge may be disposed off directly. However, because of secondary environmental impact of sludge disposal, and shortage of land, the  $\text{CaSO}_3$  is generally oxidized to calciumsulphate ( $\text{CaSO}_4$ ) that can be collected with fly ash and sold. However, environmental problems associated with mining of limestone and the disposal of solid and liquid wastes from FGD may lead to local environmental issues. (44) When magnesiumoxide is used, magnesiumsulphite that is formed is used as the starting point for cells producing sulphuricacid or elemental sulphur (45).

One of the main alternatives to the wet lime/limestone process is the Wellman Lord regenerable FGD system, which recovers elemental sulphur or sulphuricacid by using sodiumsulphite ( $\text{Na}_2\text{SO}_3$ ). As the reagent is regenerated, the raw material required is much lower for this system. However, investment costs are higher for this - which makes it less attractive to power station operators (46)

In the dry scrubbing method, final product being a dry waste is easier to control and recycle than wet sludge. This technique requires less of: human power, energy and water. But these methods have lower sulphurdioxide removal capacity and are economically less effective specially for high sulphur coal (47). Dry scrubbers can be used in two different processes. Either a lime slurry is sprayed in to the flue gas which absorbs the sulphurdioxide, or ammonia is sprayed into the gases, producing ammoniumsulphate ( $(\text{NH}_4)_2\text{SO}_4$ ) as a dry end product. This can be used as fertilizer (48).

iv) Use of Energy Conservation technique and use of Non-Conventional Energy Sources

If substitution of new technology is a theoretically possible approach to acid rain control for the supply side, then energy conservation may hold equal promise through management and demand (49). Also, suggestions have been made to use, wherever possible, nonconventional energy sources such as solar, wind, biomass, nuclear, etc. Also, 'clean' alcohol fuels (ethanol and methanol) can be used in place of gasoline based fuels. Unfortunately, each alternative source of energy has also its own environmental impact (50)

Oxides of nitrogen: i) Reduction during combustion Because oxides of nitrogen are formed by the effect of combustion of nitrogen in air, and in fuels, lowering the combustion temperature and reducing the time air stays in the combustion chamber can reduce  $\text{NO}_x$  formation. The simplest option is to modify the burner so that the fuel and air mix slowly, reducing the intensity and temperature of combustion (51). A variety of specific techniques of varying sophistication may be used. These vary from lowering the amount of excess combustion air used, through to recirculating flue gases, carrying out combustion in two stages. (52)

ii) Post-combustion control: There are many methods of flue gas denitrification, but the most commercially applied flue gas denitrification method uses selective catalytic reduction (SCR), where ammonia is added to the furnace exhaust gases and the mixture subsequently passed over a fine bed catalyst (53). The SCR is simple but expensive, as the catalysts need to be replaced every 4 -5 years. Also the catalysts used often get 'poisoned' by the lead present in the fuel used (54).

iii) Cutting vehicle emission. As the main anthropogenic source of oxides of nitrogen is road traffic, automobile exhaust is therefore a major target for emission control technology. The most widely available system is the catalytic converter. The three way converter reduces emission of oxides of nitrogen, carbonmonoxide and hydrocarbons. Fitted to the vehicle exhaust pipe, it contains either beads or a honeycomb like structure coated with a precious metal combination of platinum (85 %) and rhodium (15%). The spent exhaust gas from the engine passes through the converter, which oxidises carbonmonoxide and hydrocarbons to carbondioxide and water, and reduces oxides of nitrogen to nitrogen.

Attempts have also been made to change the design of car engines with a view to reduce emission of oxides of nitrogen (55)

Use of olefins as reductants for selective removal of oxides of nitrogen from exhaust gases, either by bleeding the olefins into the exhaust stream or by blending them into the fuel itself, has attracted the interest of engine workers and regulatory agencies. However, research has shown that the use of ethene and propene over zeolite catalyst at a temperature range of  $450-600^\circ\text{C}$  produces significant amount of hydrogen cyanide (HCN). Also a significant amount of undesirable nitrous oxide ( $\text{N}_2\text{O}$ ) is produced at temperatures

near 427 °C - a temperature around which these convertors work. A problem specially with diesel engine that can adversely affect conversion catalysts is soot in the exhaust associated with such engine (56)

iv) The electron beam technology: To circumvent the need for separate schemes to control sulphurdioxide and oxides of nitrogen, scientists have developed a Fe(II) thiochelatate complex that enhances the solubility of nitricoxide (NO) by absorbing nitricoxide to form iron nitrosyl complex. The bound nitricoxide is then converted to ammonia by electron beam technique, regenerating the active Fe (II) catalyst

Results suggest that this process can readily be integrated into existing wet limestone scrubbers for the simultaneous removal of sulphurdioxide and oxides of nitrogen. (57)

### **ACID RAIN AND INDIA**

To date, most of the research on acidification has focused on the temperate zone of the northern hemisphere. However, there is an increasing concern about the potential impact of acidification in tropical regions, especially in developing countries such as India, since such countries are increasing their energy consumption as industrialization proceeds. Biomass burning and deforestation in these regions also contribute to acidification by releasing sulphurdioxide and oxides of nitrogen to the atmosphere. While the extent of acidification has not been identified, there are some tropical countries, where acidification has been reported to have started (58)

The tropical countries can be characterized by the following major traits. (i) High daytime temperature and sunlight intensity all year long. The intensive sunlight makes many photochemical processes in the atmosphere efficient - leading to high concentration of hydroxyl radical and strong vertical mixing of air in the lowest layer of atmosphere. This implies that the air close to the surface is regularly transported to a height of 1.4 km and is replaced by air originating from such altitudes (ii) The average rainfall of the tropical countries being high, wet deposition is likely to be a major deposition mechanism for sulphur and nitrogen compounds in these regions. (iii) Wind being relatively steady in these regions with little change in direction over extended periods of time, areas downwind of continuously emitting sources of air pollution in the tropical countries experience very high average concentration and deposition over long periods and time.

iv) Wide spread bushfires, grassfires, biomass burning represent an important source of sulphurdioxide and oxides of nitrogen in the atmosphere for the tropical countries (59)

Four basic processes introduce nitrogen compounds in the tropical atmosphere –

i) emission from soil microbial process, ii) lightening ii) combustion of fossil fuel and biomass iv) ammonia volatilization. Nitrification\* and denitrification are microbial processes occurring in soil and water, which lead to the formation of oxides of nitrogen This also occurs through microbial process called chemodenitrification following the biological production of nitrites Nitrification occurs more rapidly with increasing temperature upto 35°C to 40°C (and then decreases to zero around 60°C) The rate of denitrification also roughly doubles for every 10° C rise in temperature, and is helped by high-water content of soil. Such rates are therefore high at the hot, wet, tropical soils (60)

The National Environmental Engineering Research Institute (NEERI) - situated at Nagpur, in one of their projects had studied the atmosphere chemistry of Indian urban centres. This study involved evaluation of the acid rain status in ten major cities in India, at various sites representing industrial, commercial and residential areas. These ten cities were : Ahmedabad, Mumbai, Kolkata, Delhi, Hyderabad, Jaipur, Kanpur, Kochi, Chennai, Nagpur The rainwater analysis of urban environment has indicated that the pH of the first rain after summer is always lower than that of the subsequent rain A minimum pH of 4.8 had been observed at Kochi, while the average pH varied from 6.2 to 7.6 (Table 9) High sulphates in rainwater at Ahmedabad, Hyderabad, Kanpur, Kochi can be directly correlated to industrial activities. The nitrate content in rainwater in general is found to have a low profile Thus, according to NEERI's observation, the acid rain situation, by and large, is under control in India as a whole, at least at the present time (61) (Refer also to Tables 4 and 5).

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\*Nitrification is the biological oxidation of fixed nitrogen and denitrification is the microbial process involving the reduction of nitrate ions  $\text{NO}_3^-$ , or the nitrite ions  $\text{NO}_2^-$ , or nitrousoxide  $\text{N}_2\text{O}$  to nitrogen  $\text{N}_2$  under anaerobic condition

The Taj Mahal Issue: The original controversy about the possible damage to the Tajmahal (built of marble) by acid rain\* was touched off in the 70's, by the proposal to build a sulphurdioxide spewing oil refinery at Mathura about 49 km away from the Taj Mahal at Agra, and about 40 km away from the famous Bharatpur bird sanctuary. (62)

A survey was undertaken by NEERI, which indicated that the Taj has a daily or short term average sulphurdioxide concentration of 107 microgram/cubicmetre and the highest concentration would be in December (63). NEERI's survey of Agra town had shown that more than the refinery, the Taj was threatened by the sulphurdioxide source within the town itself. Three main outlets were identified. The most serious were: the 2 - 10 MW thermal power station, the railway yard which was using coal for its locomotives adding to the smoke; as did some 250 iron foundries the main industry in the town. With the concern about the possible damage to the Taj mounting gradually, the Government of India appointed an expert committee in July '74, to examine this issue. After one of the most exhaustive studies conducted on the impact of pollutants on a monument any where in the world, the committee submitted its report in 1977. The committee explained that with the pollution control facilities planned at the Mathura Refinery, even at the most adverse meteorological conditions, the long term effects due to the Refinery would not be harmful to the Taj and there would be no need to shift the proposed Refinery from Mathura

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\* Please see pages 21 to 23 for how acid rain affects marble structures

**Table 9**  
**ACID RAIN STUDIES IN TEN CITIES OF INDIA**

CITY	pH
Ahmedabad	6.3
Mumbai	6.5
Kolkata	6.4
Delhi	6.4
Hyderabad	7.2
Jaipur	6.7
Kochi	6.2
Kanpur	7.6
Chennai	6.2
Nagpur	6.4

Source: NEERI Annual Report (1992-1993)

The Committee however recommended, the closing down of the two thermal power stations; replacing coal with diesel in the railway marshalling ground, and shifting the existing small industries - particularly the foundries to an area south east of Agra, beyond the Taj so that their emissions could not blow over the monument. Recommendations were also put forth that, no new industries should be located north West of the Taj (64). A ban was imposed on the use of diesel generators by industrial units. Standards for vehicles were prescribed under the Environmental Act. An area of 10,400 sq km - in the shape of a trapezium was created around the masoleum in 1983. (65) No new factory was to come up within this. Yet another precaution was the establishment of a green belt between Agra and Mathura. The use of coal in the refinery's power plant was advised to be deferred, till technology permitted its desulphurisation. (66).

Despite these, things did go wrong. The number of industries inside the trapezium rose from 1,500 in 1981 to 2,350 in 1993. The number of brick kilns in Agra increased from 16 in 1981 to 227 in 1993. Diesel engine manufacture stood at 1 lakh a year compared to virtually none in 1981. An increase of 25 to 100% was also reported in the number of units engaged in chemical, rubber, and other industrial activities. The number of gensets (the generators used for producing electricity these release a lot of carbon monoxide, sulphur dioxide and oxides of nitrogen) is estimated at 20,000 to 40,000 in this area. The top sources of sulphur dioxide in the vicinity of the Taj have been identified as: the Mathura refinery 38%, industries using steam and coal 15%, kilns 13%, domestic 4%, vehicles 3% (67).

A report prepared by the Regional Research Laboratory (RRL), Bhopal in 1984 had observed that the inner chamber where the grave of Shah Jehan and Mumtaz lie, faced the most serious threat because of the high humidity level that helps fungal deterioration (68).

The Mathura Refinery Project was commissioned in 1983, and around that time in 1984, a Delhi based Supreme Court lawyer took it upon himself to wage a one-man battle against the possible destruction of such a cherished edifice and moved the Supreme Court of India with his public interest litigation. After 9 years in September '93, the Court ordered the immediate closure of 212 industrial units around the Taj and another 299 units were given notice of 2 months to install devices to check pollution. Admittedly, this has led to a heated debate - is saving a piece of historic relic more important than the bread and butter of thousands of workers in these industrial units? The 'environmentalists' argue that it is a question of time before workers will fall prey to unchecked pollution and it certainly cannot be in their interest that their factories be so callous as to make money without spending some on containing toxic gases. Worse still, this may affect even those who have nothing to do with industries. Finally, the Tajmahal is as much an economic proposition, as anything else. It provides employment directly or indirectly to more than 10,000 people and half-a-million foreigners visit it every year, bringing precious foreign exchange. Also, they argue, insistence to adherence to pollution control cannot be considered anti worker or against the policy of industrialization.

A few suggestions have been put forth to help tackle the problem. The Taj trapezium must get uninterrupted power supply. This will enable those factories using coal to switch over to electricity. Also, the use of diesel generators should be restricted. Supply of gas from the Mathura refinery to the trapezium help people discard coal as a domestic fuel. Establishment of environmental friendly industries will also take care of the Taj (69). Of all these the most effective, economically viable, environmental friendly method suggested is to afforest the open area around the Taj densely with trees of the sturdy variety. This will not only shield the monument from suspended particulate matter (SPM), but will also absorb other gaseous pollutants. The Agra Development Authority has already approved a plan for a national park around the Taj. Also, the decision to relocate the three national and three state high ways running through the area of the Taj so as to reduce the effect of pollutants from the vehicles would also be an effective step. (70)

According to refinery sources, it already has built devices to limit the sulphur dioxide emission by use of low sulphur fuel, and by employing devices such as amine washing of exit gas. It also has stacks, which are 80 metres in height (71). Its current emission level is also below the standard limit of 1,000 kg/hour (72). But the nagging doubt remains, will the effluents of the Mathura Refinery, with those of the other industries in the neighborhood not corrode the Tajmahal? From all possible evidences, such a situation appears to be ruled out, especially as long as low sulphur crude is being processed here. However, the situation may change, if use of low quality crude be imposed some day due to economic reasons (73).

Another historic monument of importance that is reported to be getting damaged is the Red Fort at Delhi built of red sandstone. Pollutants emitted by the nearby Indraprastha Power station and vehicles plying on the road in front of the monument are damaging the sand stone facade. A large number of artifacts in the Fort e.g. rich zari work and textiles of the period, leather work and historic documents stored in the Archaeological museum inside the complex are getting damaged due to the high concentration of sulphurdioxide in the air. Also, many miniature paintings, kept at the two site museums have got discoloured and have become soft. Also damaged are the painted wooden ceilings in the Dewani-i-Khas. Textiles are the most vulnerable of all



(see Table 8) and are the first to get spoilt. At many places, huge slabs have become weak, presumably at the joints, where wet deposit of sulphur has seeped inside the fort's wall and weakened the red sandstone. The pollutants are also corroding the marble surface and the marble floor. However, the damage has not yet reached alarming proportions. (74)

## **WHAT ARE WE DOING TO REDUCE ACID RAIN?**

The first published reference to acid rain was dated 1872. But, as long as there has been carbon dioxide in the atmosphere, some of it has dissolved in rainwater to form carbonic acid  $\text{H}_2\text{CO}_3$  - making rainwater naturally acidic. Without the help of any human activity, nature has also made acid rain from oxides of sulphur vented by volcanoes and from other gases emitted into the atmosphere from natural sources. There is nothing new about any of these processes. What is new is that human beings have been adding significantly to acid deposition at faster and faster rates in many parts of the World. For example, although the acid rain problem correlates more to the type of use and the method of combustion of coal, than on the amount of coal used – but burning of large amounts of coal for electricity generation is a recent phenomenon. Similarly much oil and petrol have also been burnt at high nitrogen oxide generating temperatures, also in the recent decades only.

A second contributing factor to acid rain formation due to anthropogenic causes can reasonably be presumed to be the 'tall stack' strategy adopted in the –60's and the –70's. Earlier, the coal burning units used to be concerned about the effects of air pollutants like sulphur dioxide, on human health of the locality only, and thus the idea was to deal with this problem by building tall smoke stacks that will lift the pollutants up and over the population surrounding power plants. It was thought that the pollution would be sufficiently diluted by the time it came back down and no health standards would be violated. It is only recently that attention has been paid to other impacts such as formation of acid rain.

The acid rain problem itself now boils down to a few basic issues. Just how far can the constituents of acid rain travel? What exactly are the impacts of acid deposition on lakes, soils, crops, forests, living beings and the ecosystem? What level of emission control makes sense in the light of damage and the cost of emission control? What factors other than the burning of coal and oil contribute to acid pollution? Just what is the best technology to keep the oxides of sulphur and those of nitrogen out of air? (75)

Although experiments with tracer elements suggest that it may soon be possible to follow emissions from specific sources until they are deposited as acid rain, - the ingredients of acid pollution being invisible and distances traveled large, it is still not

possible to establish a visible link between the source of acid rain and the areas which suffer its effects. The pollution of acid rain therefore transcends national boundaries, creating needs for international cooperation.

The geographical distribution of acid rain is largely restricted at present to the industrialized nations of the northern hemisphere. But it has the potential to expand to a near global scale in the future. Much will depend on the rate at which the developing countries - India included, increase their rate of industrialization, and the nature of their industrialisation and urbanisation efforts (76). Also, it should not be assumed that the lower per capita emission leads to a lower degree of acidification of the atmosphere. Clearly, the size of the impact of China's population on the concentration of sulphur in the atmosphere is considerable, when compared to that of North America. Thus, countries of the developing world, which are experiencing a large increase in their population, will also experience an increase in their per capita emission of sulphur and nitrogen as they continue along the path for industrialization (77). Studies have already identified the southern peninsula of India as a potential problem area for the future .

A critical question is, what will the effect be, if these emissions from the developing world occur as predicted? Assuming that the emission to the atmosphere from North America and Europe will not subsequently increase in the future, the effects will be of two types - direct and delayed. The direct effects are those that are already in existence today. These effects will continue into the future. The delayed effects are those that are not evident today, but that will develop in the future, with continued deposition of sulphur and nitrogen from the atmosphere. (78). The effect of acidic deposit being cumulative, the damage increases each year a little more. Hence, even if emissions do not increase, acid deposition will continue to cause deterioration for some lakes, soil, etc. (79).

In 1980, the acid producing countries of the northern hemisphere had come together and had formed what is known as the '30 percent club'. The name was coined because the outcome of this meeting required the participating nations to reduce their emission of sulphurdioxide - the main cause of acid rain by 30%. On March 1, 1993, at Geneva, negotiations began for a new international treaty, to limit the damage caused to the environment by acid rain. (80). This treaty was finalised in June 1993 at Oslo,

Norway. This agreement required emission cuts based on a computer model on acidification and pollution dispersion, developed by the International Institute for Applied Systems Analysis in Austria. The emission cuts are intended to ensure that sulphur deposit will in the long term fall below critical loads. In the mean time, emission should be cut as far as possible, without entailing excessive cost. This agreement forms a new protocol under the 'Convention on Long Range Transboundary Air Pollution'. Taking 1980 as the base year, it required a definite emission cut by the end of the decade, for the currently acid producing countries viz. Germany, Sweden, Italy, U.K., U.A., Russia (81).

Individual countries are also anxious to reduce their share of acid production such as the Clean Air Act, Amendment, 1990 of the U.S.A., requires electric utilities to substantially reduce emission of sulphur dioxide and nitrogen oxides over the next 15 years. Utilities all over the U.S.A. must cut their sulphur dioxide emissions by half from the 1980 level. It also sets a permanent ceiling on the total amount of sulphurdioxide that may be emitted nationwide. So that, even as population grows and the demand for electric power rises, emissions will not increase. The law also requires most coal burning utilities to install new burner technology to reduce nitrogen oxide emission by about 30-50% (82). It has been recently reported by Britain that, the chemicals that caused acid rain and were sources of pollution in the '80-s have been nearly halved between 1991 and 2001. Switching over from coal to natural gas is attributed as the main factor. Most European eco system have now started fuel switching and flue gas treatment. A 3 way catalytic convector has also been introduced for cars in western Europe. Due to all these efforts, emission of  $\text{SO}_2$ ,  $\text{N}_2\text{O}$  and  $\text{NH}_3$  fell from 6.7m tonnes in '90 to 3.4 tonnes in 2001 (83). This decline in the  $\text{SO}_4^{2-}$  concentration has also helped in decreasing the concentration of aluminium in soil – the mobilisation of aluminium from acidic forest soil being an ecologically important consequence of acid deposition in the environment, because of its adverse effects on soil, forest vegetation and surface water.(84)

In India, although at the present time, the emission of sulphurdioxide and oxides of nitrogen are under control when compared to the acid producing countries of the west, the Central Pollution Control Board (CPCB) has prescribed a limit for these emissions keeping future developments in view. (85). The introduction of "unleaded" petrol in India

by December '97, under a Joint Action Plan of the Ministries of Environment and of Petroleum, has drastically reduced automobile exhaust pollution. As a result, not only has the level of lead in the air we breathe reduced, but the amount of many other noxious substances including oxides of nitrogen have reduced as well. Unleaded petrol also permits the automobile industry to use catalytic converters - devices fitted at the exhaust system of cars and scooters to convert the pollutants to less harmful compounds (86). As a measure to reduce acid pollution, an Integrated Coal Gasification Based Combined Cycle (IGCC) plant has already been set up by Bharat Heavy Electricals Ltd., (BHEL), Trichy. Developments of pressurized fluidized bed gasification techniques have been taken up in India for this purpose, as well. (87)

While many of the scientific and technological innovations and scientific inventions of the western countries can easily be adopted in a tropical country like ours, but such adoptions are difficult in fields of environmental sciences and engineering. Since, unlike most other fields, the parameters in these fields depend mainly on the ambient environment. The field of acid rain is no exception. Thus, to abate the acid rain problem, the Indian environmental scientists are working towards finding out methods, which are particularly suitable to Indian conditions, and are also attempting to make suitable modifications in innovations emanating from the western countries, before applying them under our field conditions.

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